To: McClintock, Katie[McClintock.Katie@epa.gov]
Cc: Johnson, Steffan[johnson.steffan@epa.gov]; Fairchild, Susan[Fairchild.Susan@epa.gov]
From: Narvaez, Madonna
Sent: Tue 2/23/2016 8:04:37 PM
Subject: FW: Questions about chromium III reactions
Linak_etal96.pdf

Here is work that the National Risk Management Lab did on chromium reactions at high temperatures. It is possible they may be able to do calculations for higher temperatures.

From: Rosati, Jacky
Sent: Tuesday, February 23, 2016 10:51 AM
To: Nunez, Carlos <Nunez.Carlos@epa.gov>
Cc: McKinney, Doug <Mckinney.Douglas@epa.gov>
Subject: Fw: Questions about chromium III reactions

FYI - we are working on this .....

Dr. Jacky Ann Rosati Rowe

Chief, Air Pollution Technology Branch (APTB)

National Risk Management Research Lab

Air Pollution Protection and Control Division

109 TW Alexander Drive, E305-01

Research Triangle Park, NC 27711

Phone 919.541.9429

Blackberry 919.597-9831

Fax 919.541.0554

rosati.jacky@epa.gov

From: Linak, Bill
Sent: Tuesday, February 23, 2016 1:49 PM

To: Lee, Chun-Wai; Rosati, Jacky
Subject: RE: Questions about chromium III reactions

CW, Jacky:

Back in the early 90s, we were interested in Cr6+ emissions from incineration, and performed modeling (equilibrium calculations) and combustion experiments to examine Cr6+/total Cr behavior in a furnace burning natural gas laced with Cr3+ and Cr6+. The publication from this study is attached.

We incinerated aqueous solutions of Cr3+ ($Cr(NO_3)_3$) and Cr6+ (CrO_3) separately and in the presence of Cl (1000 and 7000 ppm) and/or S (1000 and 7000 ppm) to examine how those constituents affect Cr speciation.

We were most interested in the possibility of forming stable $CrCl_6$ and/or $CrOCl_4$ (Cr6+) when Cl was present, and if $Cr(SO_4)_3$ (Cr3+) might be preferred if S was present. The equilibrium calculations (Fig 1) suggests that $CrCl_6$ is thermodynamically favored at low temperatures, but the presence of even small amounts of S favors $Cr(SO_4)_3$. The experimental data (Fig 3) seems to support this.

Please note that the equilibrium calculations do not predict many Cr6+ compounds (dashed curves) at high temperatures, but we did not extend our calculations above 2200 K (1900 C), higher than most peak incineration temperatures. Also, equilibrium calculations only determine the possibility of stable species, and do not include the kinetic rates of reactions to achieve equilibrium. Systems approach equilibrium, but if the reaction kinetics are slow, it may take a very long time to achieve. Chromium species considered in the calculations are listed in Table 1.

The 2800 C temperatures identified below are extremely high, but are consistent with adiabatic flame temperatures for oxy methane, ethane, or acetylene flames. We did not examine this regime, but it might be possible to form stable CrO_3 (6+) under these conditions. However, as noted on Fig 3, we burned aqueous CrO_3 and measured only small amounts of Cr6+ in the exhaust. That is, CrO_3 formed early at high temperatures likely would not survive reactions later in the post flame in a furnace environment. However, from what little I know of artisanal glass making, if CrO_3 were formed and then escaped the high temperatures and quickly quenched, it might survive into the environment even though it is not thermodynamically favored.

It's been about 25 years since we did this work. However, I will try to see if we still have a working equilibrium code and see if we might calculate equilibrium for an oxy system at 2800 C.

Bill

From: Lee, Chun-Wai
Sent: Tuesday, February 23, 2016 12:17 PM
To: Linak, Bill <Linak.Bill@epa.gov>
Subject: FW: Questions about chromium III reactions

The request from R10.

CW

From: Rosati, Jacky
Sent: Tuesday, February 23, 2016 9:31 AM
To: Lee, Chun-Wai <Lee.Chun-Wai@epa.gov>
Subject: Fwd: Questions about chromium III reactions

Can you help Rohit?

Sent from my iPhone

Begin forwarded message:

From: "Nunez, Carlos" <Nunez.Carlos@epa.gov>
Date: February 22, 2016 at 8:23:37 PM EST
To: "Rosati, Jacky" <Rosati.Jacky@epa.gov>
Cc: "McKinney, Doug" <Mckinney.Douglas@epa.gov>
Subject: Fwd: Questions about chromium III reactions

Jacky

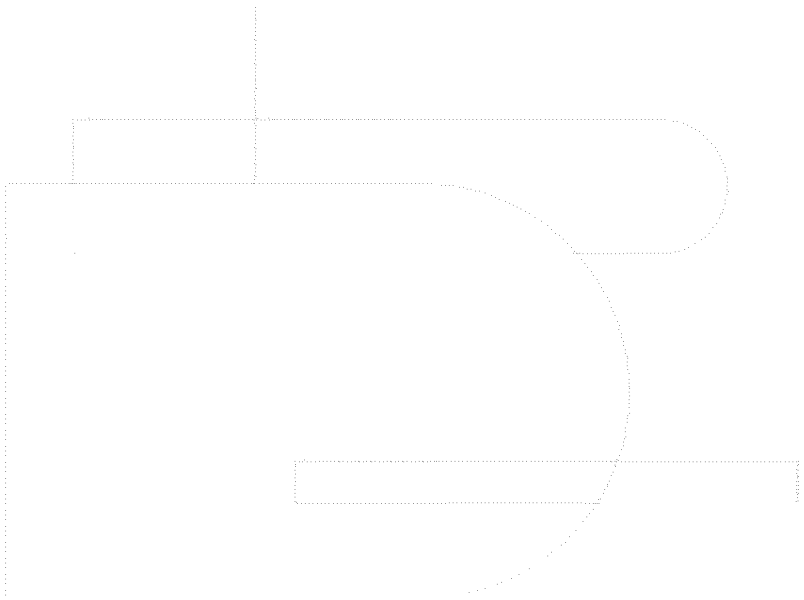
Is anyone in your branch with experience/knowledge on combustion chemistry of Cr? You can respond directly to Rohit.

Thanks!

Sent from my iPhone

Begin forwarded message:

From: "Mathur, Rohit" <Mathur.Rohit@epa.gov>
Date: February 22, 2016 at 5:42:50 PM EST
To: "Nunez, Carlos" <Nunez.Carlos@epa.gov>
Cc: "Stanek, Lindsay" <Stanek.Lindsay@epa.gov>
Subject: FW: Questions about chromium III reactions



Hi Carlos:

I received the query below. Does anyone in NRMRL work on Cr and combustion chemistry who could help?

Thanks, Rohit

From: Mathur, Rohit
Sent: Monday, February 22, 2016 5:40 PM
To: Narvaez, Madonna <Narvaez.Madonna@epa.gov>

Subject: RE: Questions about chromium III reactions

Hello Madonna:

Thank you for reaching out to us with your question on Cr. Though we have modeled Cr3 and 6 air concentrations, we have essentially treated them as inert tracers in the atmosphere. I and colleagues in my Division am not familiar with the combustion chemistry at 2800 deg C. perhaps a person more familiar with characterizing Cr emissions may know – I'll check with a few colleagues to see if they have any suggestions. You are probably already familiar with the following:

http://www3.epa.gov/airtoxics/hlthef/chromium.html

Also, there is some literature on atmospheric chemical pathways for Cr (see for example):

http://pubs.acs.org/doi/pdf/10.1021/es00001a029

Will let you know if I find anything else.

Rohit

From: Narvaez, Madonna
Sent: Monday, February 22, 2016 12:22 PM
To: Mathur, Rohit <Mathur.Rohit@epa.gov>
Subject: Questions about chromium III reactions
Importance: High

Good morning, Rohit. Anne Pope gave your name as someone who might be an expert or familiar with chromium chemistry in air. We have an art and architecture glass melting facility in Portland, Oregon where the Oregon DEQ has discovered through ambient monitoring some cadmium and arsenic hotspots within 220 meters of the facility, as well as another, smaller art glass melting facility in a different part of the city. We have since learned that the facility uses hexavalent chromium as a dry colorant, as well as trivalent chromium. The furnaces use oxyfuel to increase the temperatures needed to make the glass. They argue that as a result, the reactions are occurring in a reducing environment. They have suspended use of hex chrome and cadmium for the time being, but tell us that to stay in business, they need to start using Cr+3 again. They have not done any stack testing, so we do not know the

emissions actually coming off the furnaces. They want to show by mass balance that the Cr+3 will not result in any Cr+6 emissions. I'm not sure how that can be done, if speciated testing is not done. The monitoring the state has done showed an average of 71.5 ng/m3 of total chromium, with a couple of samples having 406 and 438 ng/m3, both on days that the company said they were not running the furnaces.

I am more familiar with the behavior of chromium in wastewater where the point is to get the C+6 converted to Cr+3, and then the Cr+3 reduced to elemental chromium. I don't know what happens if Cr+3 is subjected to 2800 degree C in the presence of oxygen. Can hexavalent chromium be a product of that reaction? I was trying to look up information but could only find the wastewater information. Thanks for your help!

==========

Madonna Narvaez

Regional Air Toxics Coordinator

USEPA, Region 10

1200 Sixth Avenue, Ste 900

MC: AWT-150

phone: 206-553-2117

fax: 206-553-0110

narvaez.madonna@epa.gov

Follow @EPAnorthwest on Twitter! https://twitter.com/EPAnorthwest